Variation in the Chemical Composition of Crude Glycerin

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ABSTRACT

The lack of knowledge about the component concentrations of crude glycerol is lmiting its use as a feedstuff. The goal of this project was to determine the concentrations of various compounds and their variation within crude glycerin. Sixteen samples of crude glycerin from biodiesel producers primarily from the Midwest were collected. The samples were procured from nine different vendors between January 2007 and February 2009 with the majority, nine of 16, being collected during October 2008. The glycerin in these samples resulted from biodiesel produced from soybean oil, canola oil, tallow, and restaurant waste. Color and viscosity of the samples varied. The pH of the samples was as follows: average = 8.25, range = 5.55 to 12.36, standard deviation (SD) = 2.06 and coefficient of variation (CV) = 24.93%. The ash concentration of the samples was: average = 4.79%, range = 1.28 to 8.98%, SD = 2.32 and CV = 48.35%. The ash was very variable due to the catalyst used in production of biodiesel and the different steps used in purifying the glycerin. Ethyl alcohol concentration was low in all of the samples (< 10 ppm). The concentration of methanol was very variable among the samples, reflective of the methanol added during the biodeisel production for formation of fatty acid esters without separation of the alcohol from the glycerin. Moisture was the next most variable in the samples (average = 6.12%, CV = 72.7%). Concentrations of fatty acids in the samples were negligible. Glycerol concentration in the samples was not very variable (average = 30.5%, CV = 1.7%). This was unexpected, especially in relationship with the variation in the other variables described; higher glycerol was expected in samples with less moisture and methanol. These data reveal that the composition of crude glycerin is quite variable, the high concentrations of methanol will limit the use of glycerin as animal feed from some sources, and the high concentrations of components other than glycerol will reduce the energy concentration of crude glycerin.

INTRODUCTION

Biodiesel is becoming a prominent alternative fuel source as the world becomes more conscientious about rising petroleum prices, decreasing fossil fuel availability, global warming, and various other pertinent issues. Biodiesel is a clean burning alternative fuel source composed of mono-alkyl esters of long-chain fatty acids derived from renewable resources, such as animal fats and vegetable oils (National Biodiesel Board [NBB], 2007). Biodiesel use would greatly benefit the environment, as emissions are lower than when conventional fossil fuels are used (Fangrui and Hanna, 1999). There are three ways to produce biodiesel from oils and fats, the cheapest of which utilizes a base catalyzed transesterification of the oil with alcohol (NBB, 2007).

The Environmental Protection Agency (EPA) lists biodiesel as a fuel, and 100% pure biodiesel has been accepted for use as an alternative fuel by the Department of Energy (DOE) and the U.S. Department of Transportation (DOT). Biodiesel can be used to power vehicles that currently have diesel engines with little or no modification (NBB, 2007).

According to the National Biodiesel Board, as of September 7, 2007, there are 165 commercial biodiesel production plants within the United States of America. The estimated production capacity from these plants is 1.85 billion gallons of biodiesel per year (NBB, 2007). For every gallon of biodiesel produced, approximately 0.34 kg of crude glycerin is created as a byproduct (Eastridge, 2007). This byproduct contains various other chemical components from the reactions used to produce the biodiesel. These compounds can consist of methanol or ethanol and catalysts like sodium or potassium hydroxide. Moisture (water) and fatty acids are also present (NBB, 2007).

The crude glycerin byproduct is not utilized by biodiesel producers. Some producers give the crude glycerin away or sell the product very cheaply to consumers. If crude glycerin proves to be useful as a feedstuff, it could be sold as another commodity (Eastridge, 2007). Currently, chemical analyses have been limited of such crude glycerin with the intention of using the byproduct as a livestock feedstuff. With the risk of feed shortages in the near future due to increasing production of ethanol fuel from corn and with the increase of biodiesel production and availability of the byproduct, the possibility of feeding crude glycerin has potential, especially if it remains on the market at low cost and is found to be nutritionally beneficial (Donkin and Doane, 2007).

Little research has been done involving feeding the glycerol to livestock. The research that has been completed involved the use of pure, food-grade glycerol, not a crude glycerin. Therefore, further research will be required if crude glycerin shows to be a feasible feedstuff. Glycerol is a colorless, sweet-tasting, sticky, odorless, and viscous substance. Glycerol or glycerin is found in many pharmaceuticals and cosmetics (Eastridge, 2007).

Recent work at the Ohio State University (Berry, 2007) found that feeding glycerol in diets containing high concentrations of non-fiber carbohydrates is not practical because glycerol is highly fermentable and can upset the rumen environment as the glycerol and grains are fermented rapidly. Work from South Dakota State University (DeFrain et al., 2004) revealed that glycerol can be given to cows as an oral drench to treat the metabolic disease ketosis. They recognized that when cows were fed glycerol, the ruminal molar proportion of propionate, a volatile fatty acid and the main precursor for glucose in cattle, increased. The concentration of another volatile fatty acid, butyrate, also increased. Butyrate is a major source of energy for ruminants. From these data, they determined that feeding glycerol may help reduce the risk for ketosis, but it is not as effective as utilizing an oral drench. Research done at the National Animal Disease Center in Iowa (Goff and Horst, 2001) also indicates that glycerol is a legitimate treatment for ketotic cattle. This research indicated that using glycerol has less toxic effects than propylene glycol, another substance used to treat ketosis. Researchers from Cornell University in Ithaca, New York have found that feeding glycerol increased the feed intake of prepartum cows (Ogborn et al., 2004). Donkin and Doane (2007) determined that feeding up to at least 15% of the dry matter content of a ration as glycerol does not have a negative effect on the cows. They also learned that a period of approximately seven days is necessary for the rumen microorganisms to adapt to the presence of glycerol in the diet. Additionally, Donkin and Doane (2007) discussed how the relative composition of crude glycerin is greatly debated.

The lack of knowledge about the component concentrations of crude glycerol is limiting the use of such a product as a feedstuff. The research that has been conducted has not answered many questions about the use of pure glycerol as a feed component and has not answered any questions about the use of crude glycerol. Before more studies can be completed using crude glycerin, compositional values need to be established. The goal of my project was to determine the concentrations of various compounds and their variation within crude glycerin. With the aid of these data, more research using this biodiesel byproduct as a feedstuff will be possible.

PROBLEM IDENTIFICATION and JUSTIFICATION

The chemical composition of crude glycerin has not been frequently determined by laboratory analysis. This lack of information is limiting the use of crude glycerin as a feedstuff for dairy cattle. The sale of crude glycerin for use in feeds would provide another source of income for biodiesel producers and could potentially make the production of biodiesel more profitable. Using crude glycerol as a feedstuff may also provide a cheaper feed alternative than corn, noting the demand and price for corn has gone up because of ethanol fuel production.

For this project, the chemical concentrations of 16 samples of crude glycerin from biodiesel producers from throughout the Midwest were analyzed for various substances. The concentrations of glycerol, total fatty acids, methanol, ethyl alcohol, moisture, and ash were determined using various laboratory procedures. Based on the amount of glycerol present in the samples, the energy and economic values will be affected. These values may be used by others for feed trials or further research to learn about the actual benefits of feeding crude glycerol.

OBJECTIVE

This Honors research project was designed to determine concentrations of various chemical compounds and their variation within crude glycerin. With the aid of these data, more research using this biodiesel byproduct as a feedstuff will be possible.

METHODS

Sixteen samples of crude glycerin from biodiesel producers primarily from the Midwest were collected. The samples were procured from nine different vendors between January 2007 and February 2009 with the majority, nine of 16, being collected during October 2008. The glycerin in these samples resulted from biodiesel produced from soybean oil, canola oil, tallow, and restaurant waste.

Ash (muffle furnace) and pH were measured in the OSU Ruminant Nutrition Laboratory. The fatty acids also were determined in our laboratory using a gas chromatograph and the procedures described by Palmquist and Jenkins (2003). Samples were sent to Barrow-Agee Laboratory (Memphis, TN) for moisture, methanol, ethyl alcohol, and total glycerin analyses. The moisture content was analyzed using the Karl Fischer titration method (AOAC, 1990). Both alcohol analyses were done using gas chromatography. Total glycerin values were measured using a titration assay (AOCS, 2006).

RESULTS

Color and viscosity of the samples varied (Figure 1). The pH of the samples was as follows: average = 8.25, range = 5.55 to 12.36, standard deviation (SD) = 2.06 and coefficient of variation (CV) = 24.93%. The ash concentration of the samples was: average = 4.79%, range = 1.28 to 8.98%, SD = 2.32 and CV = 48.35%. The ash was very variable due to the catalyst used in production of biodiesel and the different steps used in purifying the glycerin. Ethyl alcohol concentration was low in all of the samples (< 10 ppm). The concentration of methanol was very variable among the samples (Figure 2), reflective of the methanol added during the biodeisel production for formation of fatty acid esters without separation of the alcohol from the glycerin.

Moisture was the next most variable compound in the samples (average = 6.12%, CV = 72.7%). Ash was highly variable but with less variation than methanol and moisture. Concentrations of fatty acids in the samples were negligible. Glycerol concentration in the samples was not very variable (average = 30.5%, CV = 1.7%). This was unexpected, especially in relationship with the variation in the other variables described; higher glycerol was expected in samples with less moisture and methanol.

Figure 1: The variation in the color of six different crude glycerin samples is very apparent.

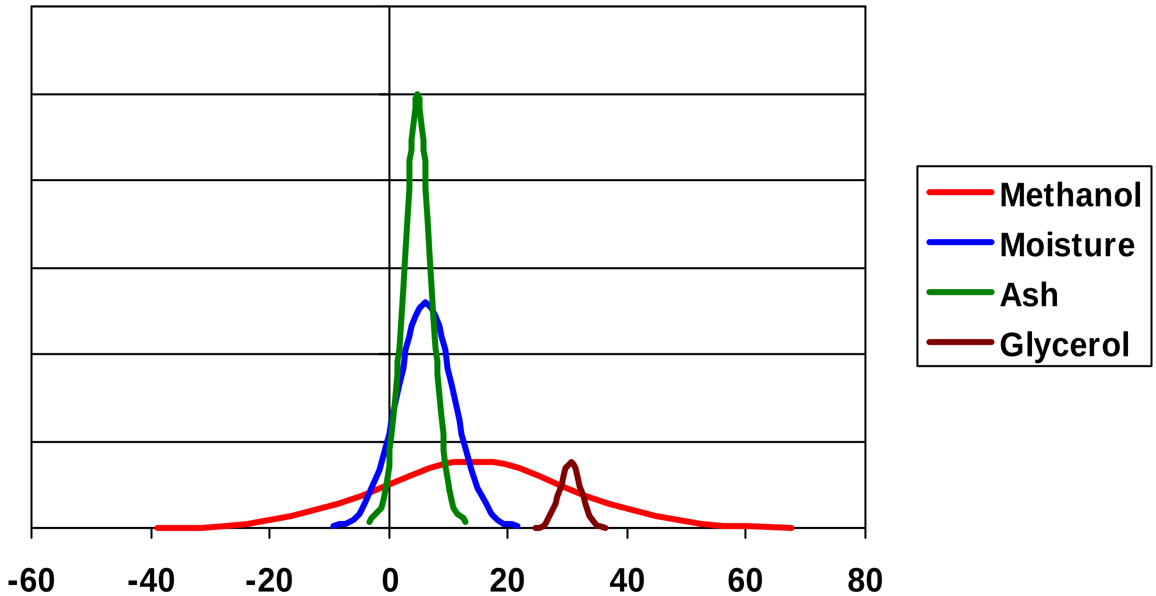

Figure 2. Distribution of various chemical components in the crude glycerin samples.

CONCLUSIONS

These data reveal that the composition of crude glycerin is quite variable, which is to be expected as the methods and ingredients used to produce biodiesel vary greatly. The high concentrations of methanol will limit the use of crude glycerin as animal feed from some sources, and the high concentrations of components other than glycerol will reduce the energy concentration of crude glycerin. Although the concentrations of glycerol were not as high as anticipated, based off of these data, crude glycerin has the potential to serve as a feedstuff with the proper monitoring of fluctuations in chemical composition, like many byproduct feedstuffs.

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